EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:
https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal ("relevant report")

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a *"preliminary report"),*
- even for experiments whose scientific area is different form the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as "relevant report(s)" in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** **Fluid-mobile element and volatile absorption during serpentine formation**	**Experiment number**: ES 705
Beamline: BM23	**Date of experiment**: from: 12.6.2018 to: 18.6.2018	**Date of report**: 17/02/2020
Shifts: **18**	**Local contact(s)**: Angelika D. Rosa	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

ROSA Angelika Dorothea[1*], Marion Louvel[2*], S. Luiginbuehl[3*], Max Wilke[4*], M. Munoz[5]

[1]European Synchrotron Radiation Facility, Grenoble, France

[2]Institute for Mineralogy, university of Muenster, Muenster, Germany

[3]Earth and Life Sciences, Free Univ. Amsterdam, Netherlands

[4]Institute for Earth Sciences, University of Potsdam, Germany

[5]Geosciences Montpellier, University of Montpellier, France

Report:

Serpentinites forming in subduction zone environments present a major sink for fluid-mobile elements at depth **[1-3].** Because of the experimental challenges, which include the low elemental concentrations and the generation of high *P/T* conditions, our knowledge on how these elements are absorbed, transported and released at depth, during the formation and stepwise breakdown of serpentine is mainly based on field observations and ex-situ fluid inclusion studies **[4,5].**

We have conducted experiments on the EXAFS beamline BM23 of the ESRF to study the uptake of the fluid mobile elements during serpentine formation, which complemented our previous results on nickel (**ES 494 and report**). We have focused in the present experiments on the elements Bromine, Rubidium and Strontium (Br, Rb, Sr). For the experiments, the X-ray beam was tuned to the energy of the K-edges of these elements (13.4737, 15.1997 and 16.115 keV) using a double-crystal fixed exit monochromator equipped with two Si(111) crystals. Beam focusing to 6 × 6 μm^2 and harmonic rejection was achieved through a Kirkpatrick Baez mirror system with Pt coating inclined to 4 mrad. EXAFS and XRF measurements were conducted in fluorescence mode using a Si SDD Vortex detector in backscattering geometry (**Figure 1**). We have refined the present setup in adding a poly-capillary collimator on the fluorescence detector which allowed to improved significantly the signal-to-noise ratio in this geometry [**6**]. To generate the high pressure and temperature conditions we used an externally heated diamond anvil cell (eRH-DAC) developed at the ESRF-sample environment that allows fine controlling of these parameters. The DAC was equipped with two full nano-polycrystalline diamonds. XRD data were acquired at 18 keV and a distance of 192 mm from the sample using a MAR164 CCD detector. XRF, XANES and XRD data were acquired at the target pressure and temperature (250 °C and 0.3 GPa) of serpentine formation in time-steps of 10 minutes to track variation of Sr concentration in the fluid and the newly formed phases.

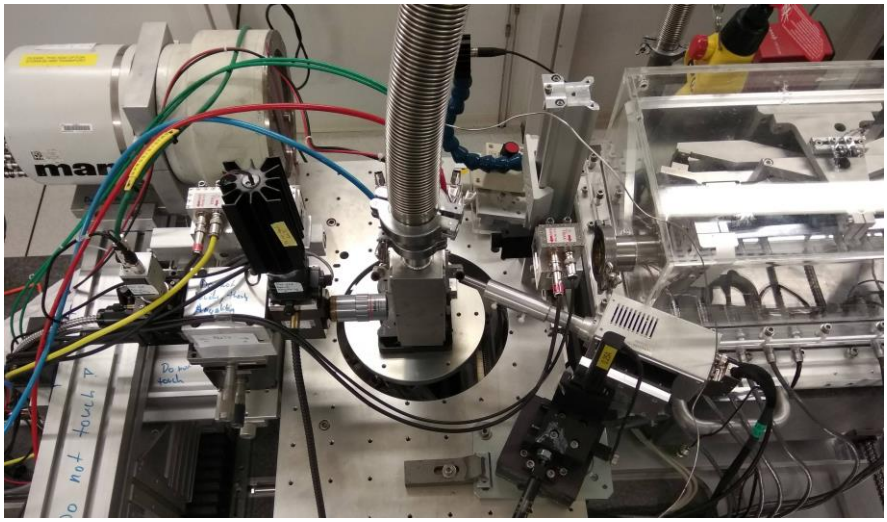

Figure 1. Experimental setup installed at BM23 to study the element uptake during serpentine formation *in-situ* at high pressure and temperature conditions. The X-ray beam is focused by the KB-system (right side). The sample was loaded in a diamond anvil cell contained in a vacuum chamber (centre). XRF data were are acquired in backscattered geometry using a Vortex detector equipped with a polycapillary. In addition XRD, Raman and XAS data were acquired in transmission geometry (left side).

The starting material consisted of a crystal of forsterite (Mg_2SiO_4) and/or enstatite ($MgSiO_3$) loaded together with a ruby crystal and either a NaBr, $RbCl_2$ or $SrCl_2$ solution containing 0.5 m NaCl and 2500 ppm of either Br, Rb or Sr. The solutions were prepared at the ESRF chemistry lab by H. Mueller in nitrogen atmosphere to avoid moister contamination. The sample pressure and temperature was than raised to 0.3 GPa and a 250 °C and held constant for more than 14 hours. Serpentine formation reaction kinetics are very sluggish but are enhanced by aluminium from one week to 36 hours **[7].** We therefore added several spheres of Al_2O_3 in the sample chamber that dissolved at this conditions in the fluid and therefore accelerated the reaction.

We have conducted four experiments in total. In a first run we observed the absorption of Sr in the newly formed serpentine crystals three hours after *P/T* stabilization (**Figure 2**). We conducted a second run on Sr-doped fluid loaded together with enstatite only. In this experiment we did not observe a reaction to serpentine at this conditions, which confirms field observations. In the experiments with Br-doped solutions a reaction between the fluid and crystal took place that induced the dissolution of forsterite. This unwanted chemical reaction suggests that Br at such concentrations leads to high fluid acidity which is inhibiting further experiments on Br doped solutions. In a third experiment Rb-doped solutions were employed. We encounter however a pressure drop during temperature stabilization, which lead to a formation of a gas bubble in the sample, inhibiting any further measurements. The present experiments remain very challenging as they involve a fluid phase with not yet fully constrained chemical properties at the target P/T conditions. In addition, the experiments require relatively low pressures but high temperatures. Upon heating the metallic gasket material may deform and plastically flow which may lead to its thinning and therefore to the opening of the cell and fluid loss.

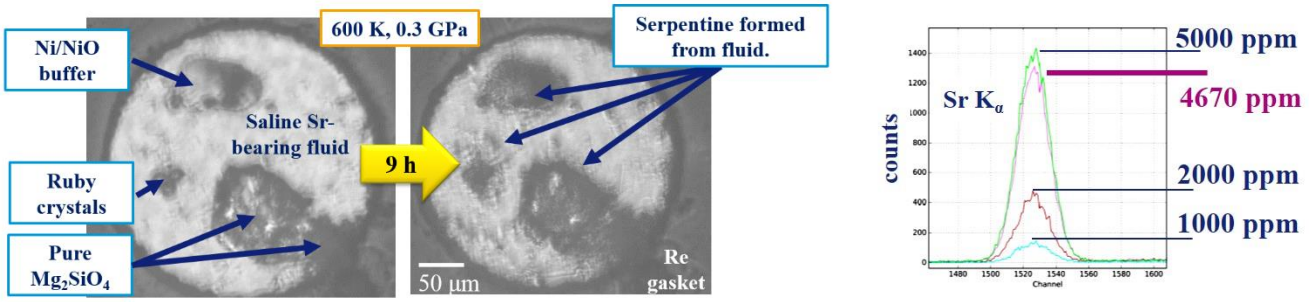

Figure 2. *Top-view on the samples contained in the Re-gasket through the diamonds at high pressure and before heating (left) and at the target P/T conditions (centre). Note, the formation of new crystals in the sample, which we identified as the serpentine variety lizardite from SEM and XRD. Figure on the right side shows XRF spectra taken in the fluid after 3 hours (pink) and compared to standard measurements (dark blue).*

To complement the *in-situ* runs we performed additionally XANES measurements on the recovered Sr-bearing serpentine samples that have been picked from the cell after quenching and fluid release. Post-mortem FEG-SEM analysis of these quenched samples revealed that the serpentine variety lizardite formed at the experimental conditions which is consistent with the *in-situ* XRD data (**Figure 3**).

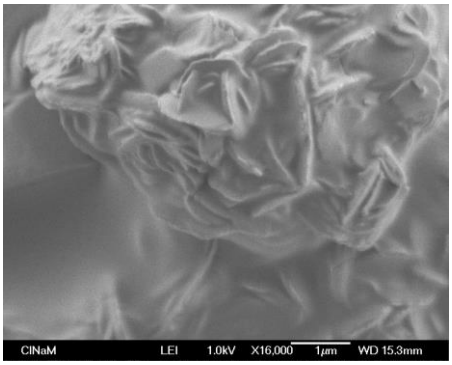

Figure 3. *FEG-SEM image of the run product. The platelets clearly indicate the formation of the lizardite variety only.*

The data on Sr uptake from newly formed serpentine have now been analysed. The XRF data revealed a minor uptake of Sr into serpentine of only 330 ppm. This is in stark contrast to our previous observations on Ni-uptake by serpentine (**ES 494 and report**) and suggest that Sr is an incompatible element in serpentine. The analysis of Sr-XANES spectra on quenched samples using full multiple scattering calculations suggested further that Sr is contained in serpentine as an intergrade SrO phase instead of being structurally incorporation into the lizardite crystal lattice (**Figure 4**).

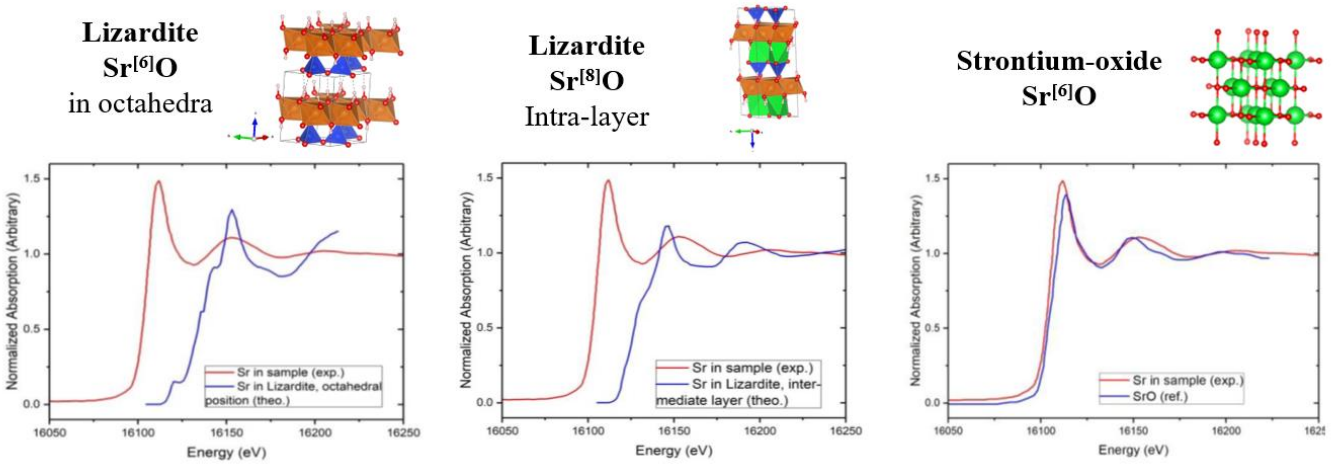

Figure 4. *Comparison of Experimental Sr-XANES spectra acquired on the recovered sample after the in-situ synthesis and simulated spectra with Sr being contained in different crystallographic sites in lizardite as well as in pure Sr-oxide.*

The new results on Sr obtained in the present experiment and those previously acquired on Ni, allow constraining the solubility of these element in serpentine and their incorporation mechanisms. These are key parameters to understand fluid element cycling in subduction zones. **The results of these two experiments (ES-494 and ES-706) are currently compiled in a manuscript that will be submitted to the journal Chemical Geology within the next months.**

Acknowledgements
We want to thanks the ESRF for allocating beamtime to this experiment and especially the staff of the beamline BM23 as well as J. Jacobs for their assistance.

References:

[1] Van Keken, et al., 2011 J. Geophys. Res., B1, 116, 2156-2202. **[2]** Deschamps et al., 2011, Terra Nova, 23, 171-178. [**3]** Deschamps et al., 2012, Chem. Geol., 312-313, 93-117. [**4]** Hattori and Guillot et al., 2007, G3, 8 (9). **[5]** Scambelluri et al., 2004, Int. Geol. Rev., 46, 7**. [6]** Tsay, A., et al., 2014. Earth Planet. Sc. Lett., 398:101-112. [**6**] Wilke et al., 2010, J. Synch. Rad., 17, 5, 699-675. **[7]** Andreani et al., 2013, Am. Min. 98, 1738-1744.